We thank the referees for the careful reading of our manuscript and the helpful comments. Below we respond to each comment point by point. The reviewer comments (in bold) are followed by dedicated answers (in black) and by modifications in the manuscript (in red).

Referee #1

This manuscript provides a clear and well-organized synopsis of the study, moving coherently from the motivation and methodology to the key seasonal contrasts, source apportionment results, and broader implications. The application of online mass spectrometry coupled with PMF is well suited to disentangling sources and seasonal variability of VOCs and OA in a street-canyon setting. The central findings—enhanced summertime OA consistent with photochemical production versus elevated wintertime nitrate, alongside distinct contributions from combustion, biogenic influences, and traffic—are communicated effectively and supported by quantitative evidence. The manuscript aligns well with the journal's scope, and I recommend its acceptance following minor revisions.

1. Lines 18-32: Please correct phrasing such as "Only little is known…" → "Little is known…". Also consider softening causal wording ("due to", "from") where attribution is inferred, and remove subjective wording such as "surprisingly little" (e.g., "relatively small").

The sentence in Lines 18-32 has been revised to improve phrasing, soften causal attribution, and remove subjective wording as suggested.

Modification in manuscript: Little is known about molecular composition and sources of air pollution in Germany's third largest city, Munich. Therefore, we investigated sources, concentrations, and seasonal variations of volatile organic compounds (VOC), semi-volatile organic aerosol (SVOA), and organic aerosol (OA) in an urban street canyon in Munich utilizing online mass spectrometry and positive matrix factorization (PMF). Organic aerosol concentrations were higher in summer (4.3 ± 2.9 µg m^{-3}) than late winter (3.3 ± 1.7 µg m^{-3}), consistent with enhanced photochemical reactions, while nitrate exhibited the opposite trend with elevated concentrations in winter (4.5 ± 3.2 µg m^{-3}) compared to summer (0.3 ± 0.2 µg m^{-3}). During summer heat, photochemistry is associated with the formation of low-volatile oxygenated OA (33 ± 20%), while aged biomass burning organic aerosol (BBOA) (25 ± 21%) associated with barbecue activities and biogenic OA (22 ± 14%) linked to nocturnal monoterpene chemistry further shape aerosol composition. The colder seasons are characterized by combustion-derived aerosols (Winter: fresh BBOA 13 ± 9%, aged 36 ± 12%; Spring: fresh 27 ± 17%, aged 37 ± 19%), whose dynamics are driven mainly by anthropogenic activity patterns. Traffic contributed at this urban kerbside relatively little to aerosol mass (5-9 %) but more to VOC (22-35%). Our findings point to efficient ways to improve air quality e.g. by reducing monoterpene emissions by urban vegetation management as well as reducing biomass burning including barbecue emissions, a major source of aerosol particles and precursor gases of secondary organic aerosol throughout the seasons.

2. Lines 24-32: Statements linking aged BBOA "from barbecue activities" and mitigation recommendations (urban vegetation management; BBQ emissions) would read more robustly if phrased as "attributed to /

consistent with / likely influenced by…", unless the manuscript later provides strong diagnostic evidence in the main text/SI.

The sentence in Lines 24–32 has been revised to adopt more cautious attribution language and to better reflect the level of supporting evidence.

Modification in manuscript: Our findings point to potential strategies to improve air quality e.g. by reducing monoterpene emissions by urban vegetation management as well as reducing biomass burning including barbecue emissions, which are attributed to a substantial fraction of aerosol particles and precursor gases of secondary organic aerosol throughout the seasons.

3. Lines 223-240: The PMF input preparation and software are described, but the manuscript would benefit from a concise summary of how the final factor numbers were selected and how rotational ambiguity was evaluated (e.g., Q/Qexp behavior, residual structure, FPEAK exploration, bootstrap/DISP if available). If these diagnostics are already in the SI, please cite them clearly in the main text.

After line 240, the following sentences have been added:

The final number of factors for each dataset was selected based on a combination of diagnostic criteria, including the evolution of Q/Q_{exp} values, inspection of scaled residual distributions, physical interpretability of factor profiles, and temporal behavior. Physical interpretability was evaluated using dominant marker compounds in each factor mass spectrum together with their temporal patterns, allowing source attribution based on established source signatures (e.g., traffic-related factors identified by toluene/xylene dominance and rush-hour diurnal peaks). Solutions with increasing factor numbers were examined to identify the point beyond which additional factors primarily resulted in factor splitting without meaningful improvement in residual structure. Detailed diagnostics, including Q/Q_{exp} evolution, residual analysis, F_{peak} sensitivity tests, and correlations with characteristic compound markers and diurnal patterns, are provided in the Supplement (Section S3.2, Figures S6 – S17, Table S4 – S9).

4. Figure 1 caption + Lines 252 onward: BLH is taken from ERA5. Please add a brief caveat that ERA5 BLH may not fully represent street-canyon ventilation, and clarify how you expect this limitation to affect the interpretation of local NO_2 and mixing (especially in winter stable conditions).

A clarification regarding the limitations of ERA5-derived boundary layer height (BLH) for representing street-canyon ventilation has been added to the Figure 1 caption.

Modification in manuscript: Figure 1: Time series of wind speed & direction 3m (above ground level) and 30 m (above ground level) in summer (a) and winter (b); temperature (T); global radiation (Ra); relative humidity (RH); precipitation; NO_2; NH_3; O_3 and boundary layer height (BLH*) in summer (c) and winter (d); Particle number size distributions; particle number of total and below 100nm ultrafine particles; $PM_{2.5}$ and PM_{10} mass concentrations; Organic aerosol (OA), sulfate, nitrate, and ammonium; Equivalent black Carbon (eBC) in summer (e) and (f) in winter; #All data plotted except the wind data were measured at the container roof. *Please note that

the BLH data refer to ERA5 reanalysis data (Guo et al., 2024), which represent large-scale boundary layer conditions and may not fully capture street-canyon ventilation or local turbulence effects.

In addition, the discussion of NO_2 and atmospheric mixing has been revised in Lines 300–309 to clarify how this limitation affects the interpretation of local pollutant accumulation, particularly under stable winter conditions.

Modification in manuscript: NO_2 concentrations were 2.5-2.8 times higher in winter/spring (26.1 ± 9.9 / 28.4 ± 10.8 µg m^{-3}) than summer (10.2 ± 7.7 µg m^{-3}) due to increased heating emissions and reduced photolysis under shallow boundary layers (339 ± 298 m /510 ± 477 m vs 516 ± 453 m, variability). The BLH values are derived from ERA5 reanalysis and represent regional-scale atmospheric mixing. They do not resolve street-canyon ventilation. In a street canyon, buildings can limit horizontal and vertical dispersion, especially under stable winter conditions. Therefore, pollutant accumulation at the measurement site may be stronger than suggested by ERA5 BLH alone. This limitation is particularly relevant for reactive pollutants such as NO_2. In addition to dispersion, NO_2 is strongly influenced by local traffic emissions and rapid photochemical processes (e.g., photolysis and O_3 titration). As a result, short-term variations in NO_2 may reflect a combination of street-canyon trapping, advection, and chemical transformation. This can differ from more inert traffic-related species such as BC, which are primarily governed by physical mixing. The ERA5 BLH should therefore be interpreted as an indicator of large-scale mixing conditions rather than street-level ventilation. The LfU station showed similar winter (27.2 ± 9.2 µg m^{-3}) and early spring (27.8 ± 9.2 µg m^{-3}) mean concentrations to Theresienstrasse, but exhibited weak temporal correlation, reflecting the strong spatial variability of NO_2.

5. Lines 257–265: The explanation combines heating emissions, reduced photolysis, shallow BLH, and then argues that higher summer BLH increases spatial differences in mean NO_2 while improving temporal correlation via synchronized photochemical cycles. This is plausible, but currently reads somewhat qualitative. Please consider adding one small quantitative check (e.g., NO–NO_2–O_3 diurnal relationships, wind-sector stratification, or a correlation/regression between BLH and inter-site NO_2 differences/correlation).

After line 315, the following sentences have been added:

The diurnal evolution of NO_2, O_3, and BLH reveals seasonally distinct coupling between photochemical processing and boundary-layer mixing (Figure S6). During summer, increasing BLH coincides with decreasing NO_2 concentrations and enhanced daytime O_3 formation, indicating efficient vertical mixing and active photochemical processing. Spring exhibits intermediate behavior, whereas winter shows weaker BLH development and persistently elevated NO_2 levels consistent with reduced photolysis and limited dispersion.

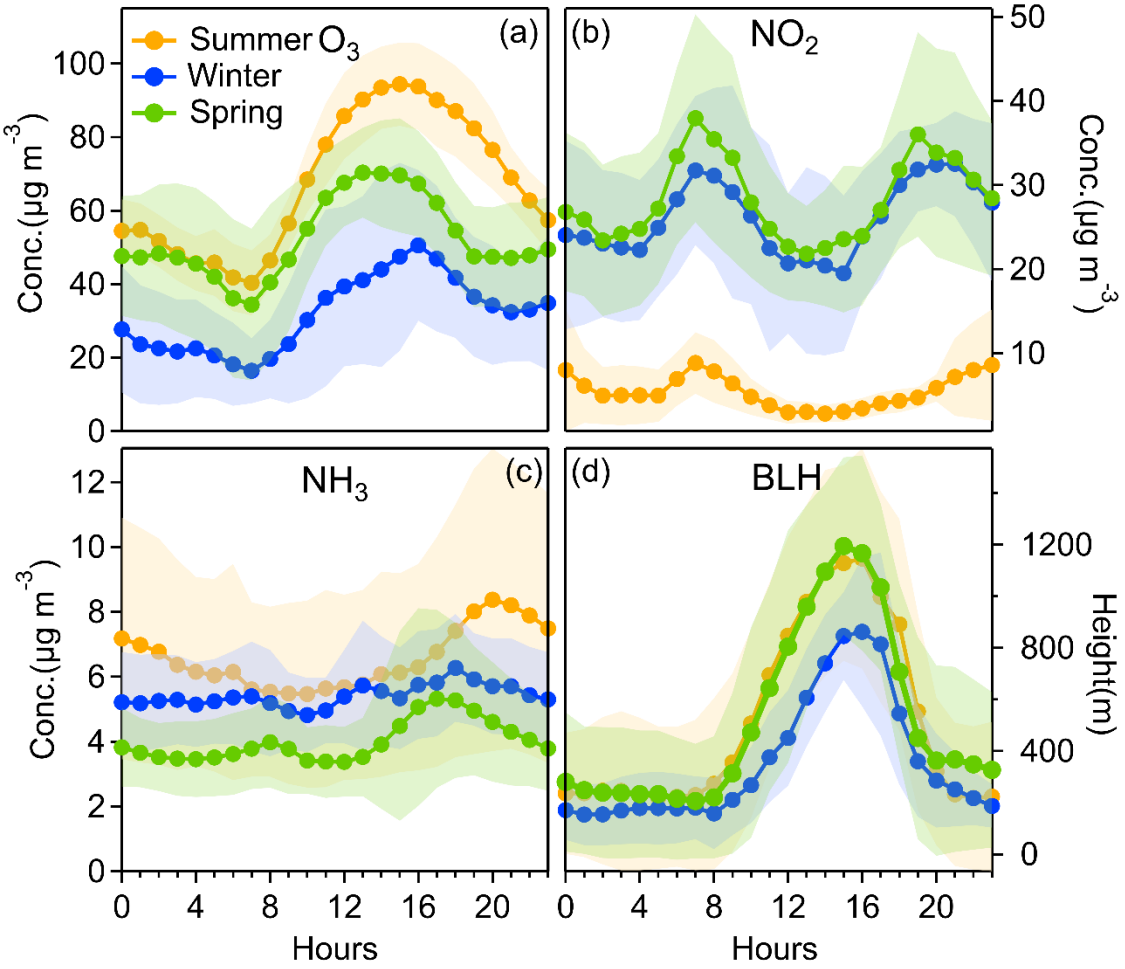


Figure S6. Seasonal mean diurnal cycles of O_3 (a), NO_2 (b), NH_3 (c), and boundary layer height (BLH) (d). Shaded areas represent ±1 standard deviation.

6. Lines 273-284: Is the attribution of elevated ultrafine particle fractions to new particle formation (NPF) adequately demonstrated? The high summertime fraction of ultrafine particles (<100 nm) is interpreted as evidence of enhanced NPF under intense photochemical conditions, but size distributions alone may also reflect primary ultrafine emissions (e.g., traffic/combustion). Please clarify whether classic NPF events were identified (e.g., emergence of a new mode, growth rates, condensation sink, event frequency). If available, include supporting information on relevant gaseous precursors (e.g., SO_2, proxies for H_2SO_4, low-volatility organic products/monoterpene oxidation chemistry, ion/cluster measurements). Alternatively, analyses stratified by weekday/weekend, wind sector, or traffic intensity indicators could help separate primary emissions from NPF and strengthen the seasonal interpretation.

Answer: We agree that particle size distributions alone do not provide sufficient evidence to unequivocally attribute elevated ultrafine particle (UFP) fractions to new particle formation (NPF), as primary emissions such as traffic or combustion may also contribute substantially. Following this suggestion, we revised the discussion in Lines 330-341 to adopt more cautious words.

Modification in manuscript: Particle size distributions revealed contrasting seasonal patterns driven by different formation mechanisms (Figures 1e-f). Summer showed the highest total particle number concentrations (10000 ± 5100 cm^{-3}) with a substantial variability dominated by ultrafine particles (< 100 nm: 80.6 ± 8.2%), indicating a strong contribution of ultrafine particles during this period. Winter exhibited lower total number concentrations (8900 ± 3500 cm^{-3}) and a lower fraction of ultrafine particles (33.6 ± 10.1%), consistent with a greater relative contribution of aged and accumulation-mode particles under stable conditions. Spring showed intermediate behavior with high ultrafine fractions (89.7%) but lower absolute number concentrations. The seasonal PM mass concentrations showed opposite trends to the particle number concentrations: winter $PM_{2.5}$ peaked at 13.0 ± 7.4 µg m^{-3} with nitrate as the dominant component due to low temperatures, shallow boundary layers and increased residential heating. In contrast, summer (6.7 ± 3.7 µg m^{-3}) and spring (4.2 ± 3.1 µg m^{-3}) showed lower $PM_{2.5}$ levels dominated by organic aerosols, despite higher particle numbers, highlighting that ultrafine particles can dominate number concentrations in urban environments while contributing comparatively little to total particulate mass.

7. Lines 495-512: You state that five OA factors are the "optimal interpretable solutions." Please briefly summarize (main text or SI reference) what alternative solutions were tested and what criteria rejected them (e.g., splitting/merging behavior, tracer correlations, residuals).

A brief description of the evaluation of alternative factor solutions has now been added to the Supplementary Information (Figure S14).

The selection of five OA factors was based on a combination of statistical diagnostics and physical interpretability. The Q/Q_{exp} value decreased progressively with increasing factor number; however, the reduction became marginal after five factors, indicating limited additional improvement in model performance. To evaluate solution stability, we examined solutions with one fewer and one additional factor. When fewer factors were used, at least one factor lacked clear correlations with characteristic compound markers and did not exhibit a physically interpretable composition, suggesting factor merging and insufficient separation of sources. In contrast, solutions with more factors resulted in two factors showing highly similar time series and mass spectral profiles, indicating factor splitting. Furthermore, correlations between factor time series and individual compounds were evaluated for all tested solutions. The five-factor solution showed consistent associations between factors and representative marker compounds, supporting meaningful source attribution. Based on these combined criteria, five factors were selected as the optimal interpretable solution.

Based on these combined criteria, five factors were selected as the optimal interpretable solution. The corresponding description has been added before Figure S14 in the SI and is referenced in the main text.

8. Lines 585-594: The correlations with BBQ charcoal combustion tracers are compelling. Please add one sentence addressing tracer specificity (BBQ/charcoal vs other combustion) and whether time patterns (evening/weekend/holiday) are consistent with grilling activity (or point to an SI figure if already done).

Answer: A sentence clarifying tracer specificity and the consistency of temporal patterns with barbecue activity has been added after line 654. The added sentence reads:

Several of these tracers are considered more specific to charcoal combustion than to traffic or fossil-fuel sources, and the pronounced evening maximum of the factor is consistent with typical barbecue activity patterns, supporting a local grilling-related origin.

Please note, that the BBOA factor shows strong correlations with charcoal combustion marker compounds, indicating a biomass-burning origin. Backward trajectory analysis combined with VIIRS fire radiative power (FRP) data for August suggests negligible influence from regional wildfires along the air-mass transport pathways. To illustrate this, we added Fig. S21 to the Supplement and included the following text in the manuscript. In addition to the classified wildfires (Fig. S21a), VIIRS also detected several fire events categorized as "unknown" sources (Fig. S21b). However, these detections exhibit very low FRP values, indicating weak fire intensity and suggesting that they are unlikely to produce sufficient emissions to explain the sustained BBOA enhancement observed in Munich during late August. This information is added to the manuscript following a corresponding comment from reviewer 2.

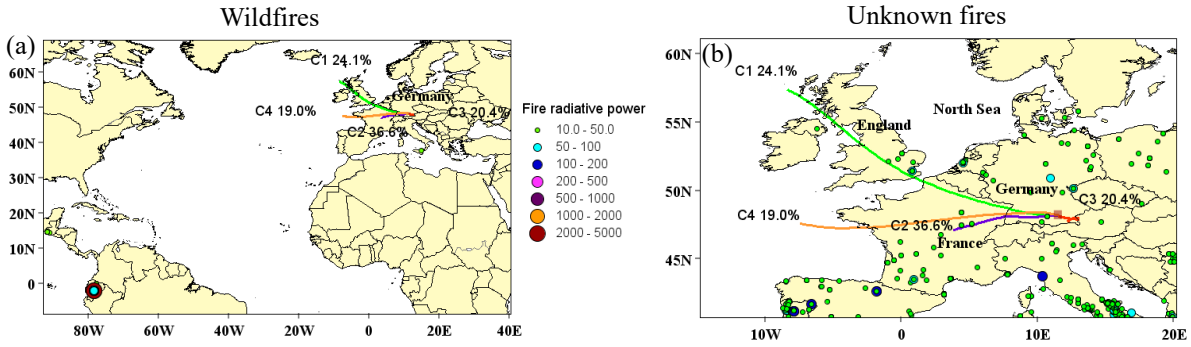


Figure S21. VIIRS satellite (https://firms.modaps.eosdis.nasa.gov/map/#d:2024-03-03;@11.9,47.3,5.7z) fire detections during August overlaid with clustered backward trajectories arriving in Munich. (a) All classified wildfires during August, colored by fire radiative power (FRP). (b) All unknown (unclassified) fire type during August, colored by FRP. The trajectory clusters (C1–C4; percentages indicate cluster frequency) illustrate the main transport pathways during the summer campaign and enable assessment of potential influence from fire activity along the air-mass histories.

9. Lines 618–623: The text implies fresh BBOA could originate from residential heating or barbecue charcoal combustion in late winter/early spring. Please clarify how you distinguish these two sources (or adjust wording to reflect uncertainty), since this affects the seasonal source narrative.

Answer: The distinction between residential heating and barbecue charcoal combustion as sources of fresh BBOA has been clarified in Lines 681–692. We expanded the discussion to describe how source interpretation is supported by correlation analyses with biomass-burning tracers while also explicitly acknowledging the associated uncertainty. Following this suggestion, we revised the discussion.

Modification in manuscript: In contrast, fresh BBOA showed strong correlations with barbecue charcoal combustion tracers: coniferyl alcohol (R=0.69), pinic acid (R=0.68), and homovanilic acid (R=0.67), as well as primary biomass burning markers including levoglucosan (R=0.72) and syringic acid (R=0.62). Notably, fresh BBOA showed weak correlation with the aged oxidation products ($C_6H_7O_5^+$ and $C_7H_9O_5^+$) that strongly correlated

with aged BBOA. This divergent correlation pattern suggests that fresh BBOA during late winter and early spring is associated with primary biomass-burning emissions, likely dominated by residential heating under weak photochemical conditions, with additional contributions from barbecue charcoal combustion as temperatures increase. Because these sources share similar biomass-burning signatures, a separation between residential heating and barbecue emissions has significant uncertainty. The observed separation between fresh and aged BBOA characteristics reflects slower atmospheric aging during colder periods compared to summer conditions, resulting in a clear separation between fresh and aged BBOA characteristics.

10. Lines 688-690: The implication that monoterpene emissions should be considered in urban vegetation management is interesting; please ensure the wording is balanced (urban green has benefits and trade-offs) and consider adding a concrete but non-prescriptive example (e.g., species selection/maintenance) or cite supporting literature more explicitly.

Answer: Following this suggestion, we added some sentences after lines 757 to balance the discussion of urban vegetation impacts on air quality and added an illustrative example of species selection together with additional supporting references.

Modification in manuscript: Consequently, monoterpene emission profiles must be treated as a critical air quality parameter and considered in urban vegetation management (Ren et al., 2014). It should be taken into account that the urban green can have positive but also negative impact on the levels of aerosol particles. Urban green infrastructure provides multiple environmental and health benefits, but may also influence secondary aerosol and ozone formation depending on species-specific BVOC emission characteristics (Ahn et al., 2022; Wang et al., 2025; Ma et al., 2025). For example, urban forestry programs can preferentially plant lower-monoterpene-emitting species such as Ginkgo biloba or Taxus cuspidata instead of high-emitting conifers such as Metasequoia glyptostroboides in NOx-rich street canyons, or adjust pruning and replacement strategies accordingly, which may help balance air-quality impacts while preserving ecosystem benefits (Maison et al., 2024).

Referee #2

Li et al. present results from measurements of organic compounds in the gas- and particle phase in a street canyon in downtown Munich, Germany, in late winter and summer. Positive matrix factorization is applied to mass spectra from PTR-MS, CHARON-PTR-TOF-MS and HR-TOF-AMS individually to find factors and identify sources of VOCs, SVOA, and OA. Based on this analysis, the authors find photochemical oxidation of biogenic emissions and biomass burning to be relevant sources for organic compounds in general, and traffic to be more relevant for VOC than OA concentrations.

Overall, this is a well written manuscript with interesting results, of relevance for air quality considerations for an urban area like Munich. As always with PMF studies, the choice of input matrices, as well as number of factors, requires detailed documentation to ensure minimum subjectivity, and this study is no exception. I have added comments where I think additional information is needed to justify certain choices made by the authors. I have several comments and questions regarding the interpretation of the BB-related factors, especially in summer. I wonder about the relevance of BBQ activities. Are there additional observations to corroborate its relevance?

I would also like to caution the authors on the summary of the paper (and this is now a potentially subjective note from this reviewer). Whereas I understand the conclusion, based on their results, that urban monoterpene emissions should be reduced, this in my opinion sends a potentially incorrect message to policy makers. The difference between winter and summer OA is within uncertainty, whereas e.g. for nitrate it is not, and PM concentrations overall are higher in winter (e.g. lines 279-284). Toxic aerosol components from traffic-related emissions such as tire and break wear, black carbon, etc. are not considered in this study. A message that urban vegetation should be controlled based on these results may potentially be misleading and could only be made after consideration of the entirety of PM2.5 or PM10 mass in Munich.

Overall, I am in favor of eventual publication of this manuscript once comments have been addressed.

L. 101-105: Please clarify what data/measurements/instruments were used for this comparison. Was it the Fidas? Did you get closure with AMS+BC measurements?

Answer: The $PM_{2.5}$ comparison was based on measurements obtained with the FIDAS. In addition, consistency between bulk $PM_{2.5}$ mass and chemically resolved measurements was evaluated by comparing AMS-derived non-refractory $PM_{2.5}$ together with equivalent black carbon (eBC) to $PM_{2.5}$ trends. The measurements showed good agreement in temporal variability (Figure e and f), supporting overall mass consistency. The instrument description has been clarified in the revised manuscript (Lines 100-102):

Modification in manuscript: The $PM_{2.5}$ concentrations at Theresienstrasse were measured using a FIDAS 200 optical particle spectrometer (Palas GmbH, Germany) and are comparable to those observed at the regulatory monitoring station Munich/Stachus operated by LfU.

L. 114-116: Please revise wording, the two measurement periods in March are clearly not during "distinct seasons". It would be good to clearly show with data how the separation between late winter and spring was determined. The separation into late winter and spring is not evident for me from Figure 1 (where I

assume the horizontal dotted line indicates the separation, however this is not mentioned in the figure caption).

Following the reviewer's suggestion, the text has been revised to clarify how the late-winter and spring periods were defined, as shown below.

Modification in manuscript: Field observations were conducted during three meteorological periods: summer (3rd-29th August 2023), late winter (1st-8th March 2024), and spring (9th-27th March 2024). The separation between winter and spring periods was based on observed transitions in ambient temperature and chemical composition, including systematic changes in organic aerosol and nitrate concentrations observed in the time series (Figure 1d and Figure 2), indicating a shift from colder, nitrate-favored conditions to warmer conditions associated with enhanced photochemical activity. Spring conditions were characterized by higher solar radiation and an increased relative contribution of organic aerosol (Figure 1d and Figure 2), reflecting stronger photochemical production. These periods therefore represent meteorologically and chemically distinct regimes rather than strict calendar-based seasonal classifications.

Figure 1: Time series of wind speed & direction 3m (above ground level) and 30 m (above ground level) in summer (a) and winter (b); temperature (T); global radiation (Ra); relative humidity (RH); precipitation; NO2; NH_3; O_3 and boundary layer height (BLH*) in summer (c) and winter (d); Particle number size distributions; particle number of total and below 100nm ultrafine particles; $PM_{2.5}$ and PM_{10} mass concentrations; Organic aerosol (OA), sulfate, nitrate, and ammonium; Equivalent black Carbon (eBC) in summer (e) and (f) in winter; #All data plotted except the wind data were measured at the container roof. *Please note that the BLH data refer to ERA5 reanalysis data (Guo et al., 2024), which represent large-scale boundary layer conditions and may not fully capture street-canyon ventilation or local turbulence effects. The vertical dotted line marks the transition between the late-winter and early-spring periods, defined based on observed changes in temperature, solar radiation, and aerosol chemical composition.

L. 148: Would you not expect a diel cycle of gas-phase background based on concentrations and temperature/RH? Please elaborate. Were the weekly background checks done during different times of the day? How variable was the background? Please add more information to the supplement.

We agree that additional clarification is needed. The text in the manuscript has been revised as follows.

The instrumental background was determined weekly at noon by introducing pure dry nitrogen (N_2, 99.9999%) into the inlet for 5–15 min to exclude ambient air and quantify the instrumental baseline (Figure S4).

The instrumental background was determined weekly by introducing pure nitrogen (N_2, 99.9999%) into the inlet for 5-15 min, during which ambient air was completely excluded. The measured signal therefore represents the instrumental baseline rather than atmospheric background concentrations and is not expected to exhibit diel variability associated with ambient temperature or relative humidity.

Instrumental background measurements were performed for all detected ions. For clarity, Fig. S4 presents selected representative ions with relatively high ambient signal intensities, including m/z 59 (acetone-related ions), m/z 93 (toluene-related ions), m/z 121 (trimethylbenzene-related ions), and m/z 137 (monoterpene-related ions). These ions were chosen to illustrate background stability across different chemical classes commonly observed during the campaign.

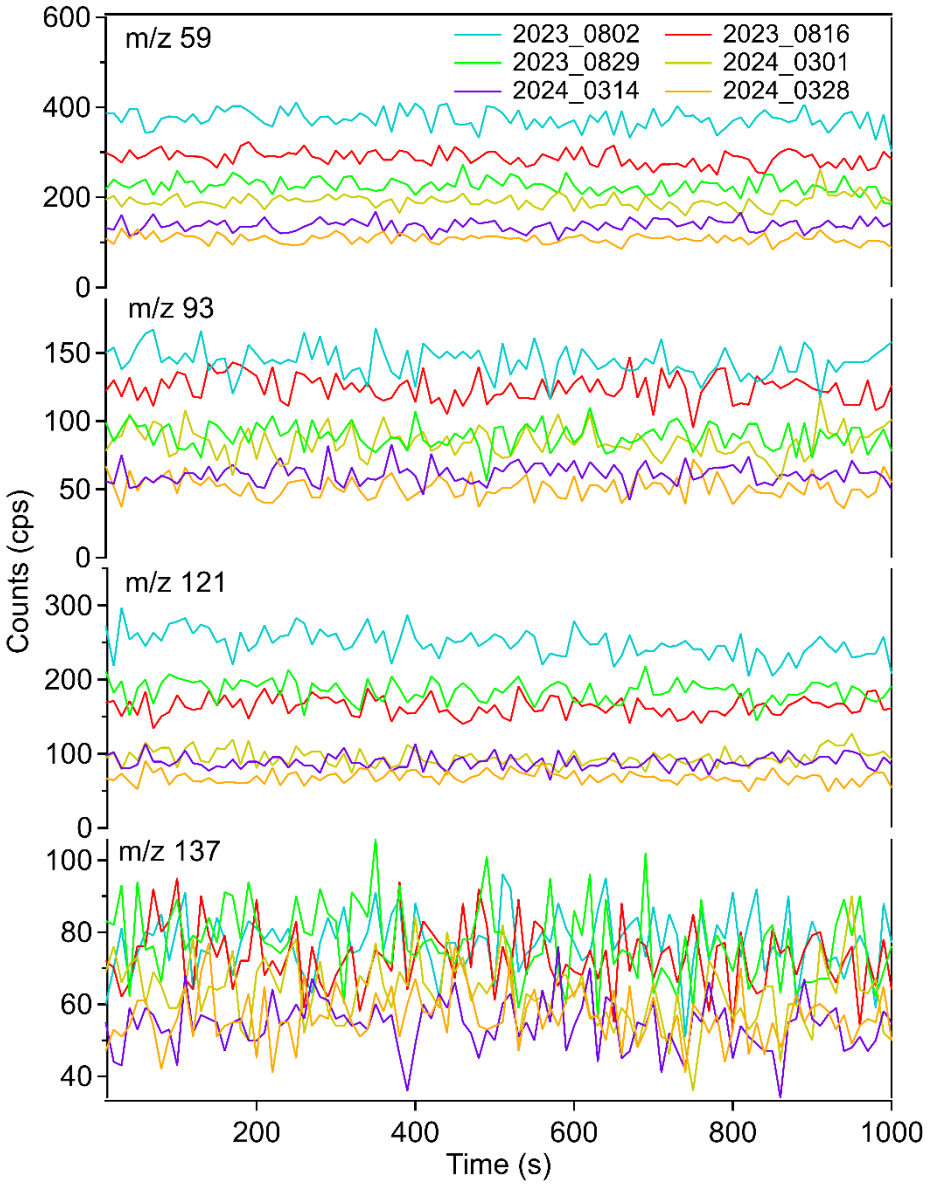


Figure S4. Instrumental background signals measured during weekly nitrogen background tests for selected representative ions. Background measurements were conducted for all detected ions; ions shown here (m/z 59, 93, 121, and 137) were selected as examples due to their relatively high ambient signal intensities and representation of different chemical classes. The small variability demonstrates stable instrumental baseline conditions throughout the campaign.

L. 223-226: Please state clearly that PMF was run separately for the three different datasets and seasons (at least this is how I understand it). Please motivate this choice and motivate why e.g. PMF was not run on the entire combined dataset, or for one instrument and all seasons. Refer to diagnostics etc. in the supplement where needed.

Answer: We clarified this point by revising the manuscript in Lines 242–256 to explicitly state that PMF was performed separately for each dataset and measurement campaign and to provide the methodological justification for this approach, as detailed below.

To investigate the sources of VOCs, SVOA, and OA, positive matrix factorization (PMF) was applied separately to (i) VOC mass spectra measured by PTR-MS, (ii) semi-volatile aerosol species measured by CHARON-PTR-MS, and (iii) OA measured by HR-TOF-AMS. PMF analyses were conducted independently for each dataset and measurement campaign rather than using a combined dataset. Separate analyses were chosen because the campaigns were performed in different seasons under substantially different atmospheric conditions and instrument states. PMF assumes temporally stationary factor profiles and comparable uncertainty structures within a dataset; these assumptions are not fulfilled when combining measurements across seasons with distinct source contributions and atmospheric processing regimes. In addition, VOC and SVOA datasets were analyzed separately because they represent chemically and physically distinct phases with different atmospheric processing timescales, variability patterns, and measurement uncertainty structures. Combining these datasets in a single PMF analysis would violate the assumption of consistent covariance structure and could lead to mixed or non-interpretable factors. Diagnostic evaluations supporting solution stability and factor selection for each dataset are provided in the Supplement (Figs. S8-S20).

L. 275: Suggest toning this down, as the number of particles <100 nm is not a good indicator for NPF.

Summer showed the highest total particle number concentrations (10000 ± 5100 cm^{-3}) with a substantial variability dominated by ultrafine particles (< 100 nm: 80.6 ± 8.2%), indicating a strong contribution of ultrafine particles during this period.

L. 318: Please specify which ions were excluded (especially the large signal ones)

Answer: We clarified this point by revising Line 318 to explicitly specify which high-abundance and low-signal ions were excluded from the PMF analysis and to provide representative examples of the excluded ions, as detailed below.

Modification in manuscript: We included 117 VOC ions (Table S2) for PMF analysis in summer and 97 VOC ions (Table S3) in winter/spring. Ions with extremely high signal intensities that could disproportionately influence the PMF solution, as well as very low signal ions with minimal contribution, were excluded. The excluded high-abundance ions are common hydrocarbon and oxygenated VOC fragments, such as m/z 33.034 ($C_1H_5O^+$), 41.039 ($C_3H_5^+$), 43.054 ($C_3H_7^+$), 45.034 ($C_2H_5O^+$), 57.070 ($C_4H_9^+$), and 59.049 ($C_3H_7O^+$). These ions were removed because their high concentrations may lead to over-representation of specific factors, whereas low-signal ions were excluded to reduce noise interference (Song et al., 2024).

L. 350-355: What is a potential activity where biomass is being burnt in summer in Munich? Please clarify. Is there an option of wildfire influence? The time series shows a clear increase in late August.

Answer: The BBOA factor shows strong correlations with charcoal combustion marker compounds, indicating a biomass-burning origin. Backward trajectory analysis combined with VIIRS fire radiative power (FRP) data for August suggests negligible influence from regional wildfires along the air-mass transport pathways. To show this we added Fig. S21 to the supplement and added the following text to the manuscript:

The BBOA factor shows strong correlations with charcoal combustion marker compounds, indicating a biomass-burning origin. Backward trajectory analysis combined with VIIRS fire radiative power (FRP) data for August suggests negligible influence from regional wildfires along the air-mass transport pathways (Fig. S21a). Although several fire detections classified as "unknown" sources were observed (Fig. S21b), their FRP values were very low, indicating weak fire intensity and suggesting that they are unlikely to contribute substantially to the elevated BBOA levels observed in Munich.

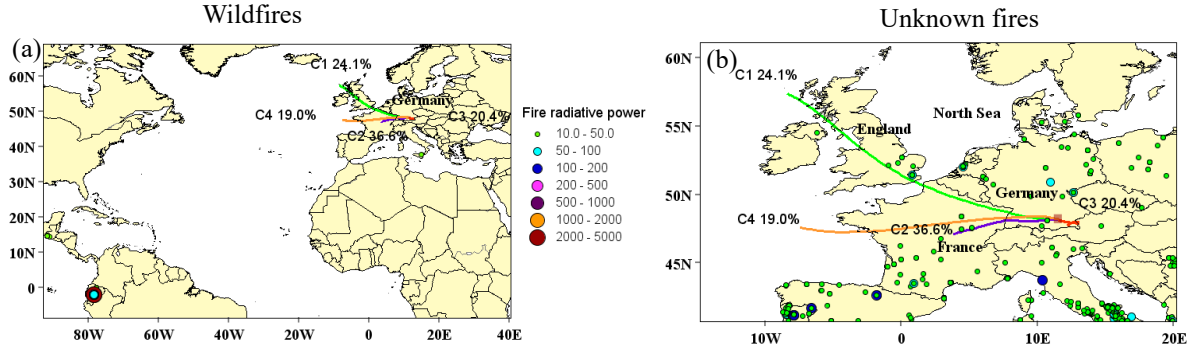


Figure S21. VIIRS satellite fire detections (https://firms.modaps.eosdis.nasa.gov/map/#d:2024-03-03;@11.9,47.3,5.7z) during August overlaid with clustered backward trajectories arriving in Munich. (a) All classified wildfires during August, colored by fire radiative power (FRP). (b) All unknown (unclassified) fire type during August, colored by FRP. The trajectory clusters (C1–C4; percentages indicate cluster frequency) illustrate the main transport pathways during the summer campaign and enable assessment of potential influence from fire activity along the air-mass histories.

L. 362-365: Why would this not be a source in summer?

Answer: This source is also expected to be present in summer. In the PTR-MS PMF results, species related personal care products like limonene and biogenic monoterpenes can partially overlap because PTR-MS provides limited chemical specificity for separating individual monoterpene isomers, which may complicate factor interpretation. However, the summer diurnal pattern shows a single, pronounced peak in the very early morning (Fig. 4), which is more consistent with biogenic/plant-related emissions and boundary-layer dynamics rather than a traffic-like pattern. In contrast, the winter diurnal profile exhibits two peaks resembling the traffic diurnal variation (Figure S10c), supporting a stronger influence from anthropogenic activities in winter. Therefore, we interpret this factor as more plant-influenced in summer, whereas in winter it is mainly associated with personal care product–related limonene.

L. 371-373: Would cooking and outdoor grilling really be an activity in winter? Would this not rather be from residual heating? How do the two biomass burning factors for winter and summer compare in detail? Why is BBOA so high in late winter?

Answer: The Lines 371–373 refer to the summer VOC factor analysis rather than winter conditions. Biomass burning emissions in winter are instead interpreted as mainly originating from residential heating.

In summer, PTR-MS detected several markers associated with charcoal combustion and outdoor grilling activities, including formaldehyde (R=0.80) (Kabir et al., 2010), coniferyl alcohol ($C_{10}H_{13}O_3^+$, R=0.90), pinic acid ($C_9H_{15}O_4^+$, R=0.76), and homovanilic acid ($C_9H_{11}O_4^+$, R = 0.83) (Vicente et al., 2018). The consistently strong correlations (R > 0.75) indicate that the aged BBOA factor in summer is strongly influenced by barbecue-related charcoal and wood combustion, which is typical for outdoor cooking activities during warm periods.

In contrast, during winter the BBOA factor shows no significant correlation with these barbecue-related tracers. Instead, strong correlations are observed with guaiacol oxidation products, including $C_6H_7O_5^+$ (R=0.80) and $C_7H_9O_5^+$ (R=0.74), suggesting emissions from residential biomass heating followed by atmospheric aging (Kodros et al., 2020).

The elevated BBOA concentrations observed in late winter coincide with persistently low temperatures (Fig. 1) and air masses arriving predominantly from Czechia, Austria, and northern Italy (Fig. S22). These conditions are consistent with the regional influence of residential heating emissions and their transport to the measurement site, contributing to the observed increase in aged BBOA.

L. 399: Did you mean 171 SVOC compounds?

Answer: Yes, thank you for pointing this out. We meant 171 SVOC compounds, and this has been corrected in the revised manuscript.

Modification in manuscript: We included 153 SVOA ions (Table S6) for PMF analysis for summer and 171 SVOA ions (Table S7) for winter/spring, excluding abundant ions that could skew results and very low ion signals with minimal impact (Song et al., 2024).

L. 429 -430: Do you see a difference between weekends and weekdays? I have a hard time imagining that this could be a relevant source during weekdays. Also, do you see compounds related to cooking? Would people not rather use coal for BBQing? Also here, this factor increases in late August – contribution from a wildfire episode?

Answer: A clear weekend–weekday contrast is not distinguishable in this dataset, likely because the measurement campaign coincided with the summer holiday period, during which typical weekly activity patterns are less pronounced.

As discussed in the response to Lines 371-373, several chemical markers associated with charcoal combustion and outdoor cooking were identified, supporting the interpretation of this factor as primarily related to local barbecue activities during summer. PTR-MS detected compounds commonly linked to charcoal and wood combustion rather than typical indoor cooking emissions.

Regarding fuel type, charcoal combustion is consistent with the observed chemical signatures, which differ from those expected for other cooking-related sources.

As discussed in the response to Lines 350-355, the increase of this factor in late August is unlikely to be related to wildfire influence. VIIRS satellite observations for August 2023 show no wildfire activity along the air-mass transport pathways reaching the measurement site. Therefore, long-range transport from wildfire events is not supported by the available evidence.

L. 453-458: If it was cooking, should this factor not be around year-round? Oleic acid and palmitic acid can also be from the users handling the instrument, has this been investigated?

Answer: Cooking organic aerosol (COA) was detected during both the August 2023 and March 2024 campaigns (Fig. 7), indicating that this source is present across seasons rather than being limited to a specific period.

Oleic acid and palmitic acid can in principle originate from human handling; however, contamination from instrument operators is unlikely in this study. All instruments were housed inside a sealed measurement container and continuously sampled ambient air through closed inlet tubing systems. The measurement setup operated largely unattended, with personnel accessing the container only during brief weekly maintenance visits. Because the sampling inlets were continuously connected to the tubing and not exposed to indoor air during operation, direct influence from instrument handling is considered negligible.

L. 500: In SVOC PMF, cooking was only identified in winter. Please elaborate.

Answer: We clarified this point by expanding the discussion around Line 500 to explain why a cooking-related factor was only resolved in the SVOA PMF during winter. The revised text now explains that, although fatty-acid-related ions were observed in summer, the higher abundance of biogenic oxidation products in overlapping mass spectral regions likely reduced the statistical separability of a distinct cooking factor in the PMF solution, leading to partial mixing with secondary organic components. The following sentences have been added after Line 547 to explain this:

Although cooking-related SVOA ions were present during summer, the higher contribution of biogenic oxidation products in overlapping mass spectral regions likely reduced the statistical separability of a distinct cooking factor in the SVOC PMF analysis (Zhu et al., 2018; Coggon et al., 2024).

Importantly, this difference does not affect the overall source apportionment results, as cooking organic aerosol (COA) was consistently identified in the OA PMF analysis for both the August 2023 and March 2024 campaigns (Fig. 7), confirming the presence of cooking emissions in both periods.

L. 553-555: See previous comments on summer BBOA

Answer: This comment is addressed in our responses to Lines 350–355 and 371–373. Briefly, the summer BBOA factor is interpreted as being primarily influenced by barbecue-related charcoal combustion based on characteristic

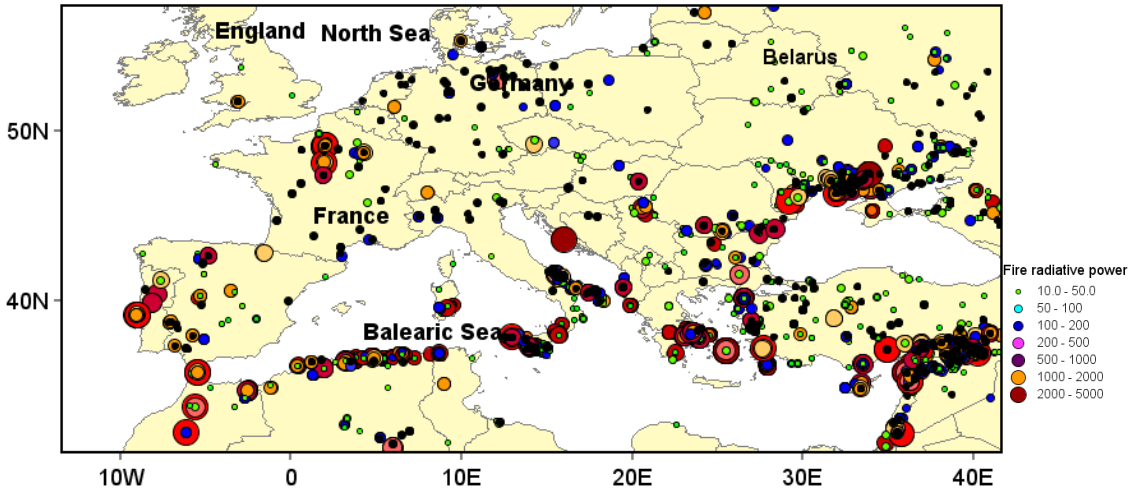
chemical tracers and correlation analysis, whereas winter BBOA is associated with residential heating emissions supported by distinct tracer compounds and diurnal behavior.

Chapter 3.3: I am still not convinced the summer BBOA is not from wildfires, as in summer 2023 there were many wildfires in Europe. Please consider this as a source again.

Answer: Following the reviewer's suggestion, we re-examined the potential contribution of wildfires to the summer BBOA factor using satellite fire observations. VIIRS fire detection data for Europe in 2023 indicate that most wildfire activity occurred during June and July, particularly in regions such as Spain, Portugal, and southern France (see figure below).

During the August 2023 measurement period, however, satellite observations show no significant wildfire activity along the air-mass transport pathways influencing the measurement site. Therefore, long-range transport of wildfire emissions is not supported by the available satellite and trajectory evidence.

Based on this analysis, wildfire influence is considered unlikely to be a dominant source of the observed summer BBOA, and the attribution to local barbecue-related biomass burning remains the most consistent explanation.



Wildfires in July.

L. 644: do you see influence from coal burning emissions?

Answer: Coal combustion can produce a range of polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs, which are often used as fuel-specific tracers to distinguish coal from biomass burning emissions. In the present CHARON-PTR-MS measurements, characteristic PAHs such as naphthalene or related oxidation products were not observed, whereas oxidized phenolic ions (e.g., $C_6H_7O_5^+$ and $C_7H_9O_5^+$), which are commonly associated with lignin combustion in biomass burning, were detected. Therefore, while residential heating emissions are supported by the observations, the available measurements suggest a stronger biomass-burning signature and do not provide clear evidence for a distinct coal combustion contribution.

Technical comments

L. 44/45: Put manufacturer in brackets after instrument name. Commonly PM_1. Specifically mention if $PM_{2.5}$ lens was used.

Modification in manuscript: The high-resolution time-of-flight Aerodyne aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Research Inc., Billerica, MA, USA) quipped with a $PM_{2.5}$ aerodynamic lens is used for the online characterization of non-refractory $PM_{2.5}$.

L. 48: More correct: "PMF of AMS datasets" cannot specify sources

Modification in manuscript: Positive matrix factorization (PMF) analysis of AMS datasets can quantitatively resolve major primary organic aerosol (POA) sources, …

L. 56-57: What is meant by "qualitatively and quantitatively"? Please clarify.

Indeed this is misleading.

Modification in manuscript: Furthermore, the CHARON-PTR-MS (Chemical Analysis of Aerosol Online Particle Inlet coupled to a PTR-TOF-MS) is a continuous measurement technique capable of providing molecular-level chemical characterization and time-resolved quantification of semi-volatile organic aerosol components.

L. 58 -59: How does CHARON-PTR-MS minimize thermal decomposition and ionization-induced fragmentation, compared to what technique? Please specify.

Modification in manuscript: CHARON-PTR-MS enhances the detection of detailed SOA chemical composition data by minimizing thermal decomposition and ionization-induced fragmentation compared to AMS employing high-temperature vaporization and electron-impact ionization. This is achieved through lower thermal stress during particle evaporation at reduced pressure and softer chemical ionization via proton-transfer reactions, which better preserves molecular information.

L. 63: Should read "in downtown Karlsruhe"

Modification in manuscript: A study in downtown Karlsruhe (southwest Germany) demonstrated that secondary oxygenated OA comprised over 60-75% of total OA throughout the year,

L. 70-72: Sentence structure needs revision

Modification in manuscript: These findings underscore the necessity for site-specific OA and VOC source apportionment studies in major European cities such as Munich in southern Germany. Although secondary formation processes consistently dominate regional OA burdens, the underlying VOC precursors, and primary emission contributions exhibit substantial spatial and temporal variability.

L. 96: Air pollution is very general here, I assume you mean organic aerosol.

Modification in manuscript: It remains unclear how much anthropogenic and biogenic sources contribute to organic aerosol (OA) in Munich and what is the fraction of biomass burning aerosol from residential wood combustion versus barbecue activities.

L. 175: How come you give as range for lens transmission 70-500 nm when you have a $PM_{2.5}$ lens? Please clarify.

Answer: Indeed, this was misleading. The AMS has a PM2.5 lens (70-2500 nm). Therefore, the text was modified as follows:

Modification in manuscript: The AMS was calibrated using dried ammonium nitrate aerosol particles with sizes of 100-500 nm to determine ionization efficiency and instrument response. Calibration particles were size-selected using a DMA, and signal stability was verified prior to and during each measurement period.

L. 198: Right bracket missing

Modification in manuscript: (Rametrics Inc., Type: LR111-ESS-D200, named KASCAL).

L. 242: If "distinct seasons" are kept above, I would refer here rather to "three campaigns"

We thank the reviewer for this suggestion. The term "distinct seasons" has been removed and revised accordingly in the manuscript.

Reference:

Ahn, J.-W., Dinh, T.-V., Park, S.-Y., Choi, I.-Y., Park, C.-R., and Son, Y.-S.: Characteristics of biogenic volatile organic compounds emitted from major species of street trees and urban forests, Atmospheric Pollution Research, 13, 10.1016/j.apr.2022.101470, 2022.

Coggon, M. M., Stockwell, C. E., Xu, L., Peischl, J., Gilman, J. B., Lamplugh, A., Bowman, H. J., Aikin, K., Harkins, C., Zhu, Q., Schwantes, R. H., He, J., Li, M., Seltzer, K., McDonald, B., and Warneke, C.: Contribution of cooking emissions to the urban volatile organic compounds in Las Vegas, NV, Atmospheric Chemistry and Physics, 24, 4289-4304, 10.5194/acp-24-4289-2024, 2024.

Kabir, E., Kim, K. H., Ahn, J. W., Hong, O. F., and Sohn, J. R.: Barbecue charcoal combustion as a potential source of aromatic volatile organic compounds and carbonyls, J Hazard Mater, 174, 492-499, 10.1016/j.jhazmat.2009.09.079, 2010.

Kodros, J. K., Papanastasiou, D. K., Paglione, M., Masiol, M., Squizzato, S., Florou, K., Skyllakou, K., Kaltsonoudis, C., Nenes, A., and Pandis, S. N.: Rapid dark aging of biomass burning as an overlooked source of oxidized organic aerosol, Proc Natl Acad Sci U S A, 117, 33028-33033, 10.1073/pnas.2010365117, 2020.

Ma, J., Wang, S., Chen, G., Zhu, S., Wang, P., Chen, J., and Zhang, H.: Estimating emissions of biogenic volatile organic compounds from urban green spaces and their contributions to secondary pollution, Environmental Science: Atmospheres, 5, 129-141, 10.1039/d4ea00099d, 2025.

Maison, A., Lugon, L., Park, S.-J., Baudic, A., Cantrell, C., Couvidat, F., D'Anna, B., Di Biagio, C., Gratien, A., Gros, V., Kalalian, C., Kammer, J., Michoud, V., Petit, J.-E., Shahin, M., Simon, L., Valari, M., Vigneron, J., Tuzet, A., and Sartelet, K.: Significant impact of urban tree biogenic emissions on air quality estimated by a bottom-up inventory and chemistry transport modeling, Atmospheric Chemistry and Physics, 24, 6011-6046, 10.5194/acp-24-6011-2024, 2024.

Ren, Y., Ge, Y., Gu, B., Min, Y., Tani, A., and Chang, J.: Role of management strategies and environmental factors in determining the emissions of biogenic volatile organic compounds from urban greenspaces, Environ Sci Technol, 48, 6237-6246, 10.1021/es4054434, 2014.

Song, J., Saathoff, H., Jiang, F., Gao, L., Zhang, H., and Leisner, T.: Sources of organic gases and aerosol particles and their roles in nighttime particle growth at a rural forested site in southwest Germany, Atmospheric Chemistry and Physics, 24, 6699-6717, 10.5194/acp-24-6699-2024, 2024.

Vicente, E. D., Vicente, A., Evtyugina, M., Carvalho, R., Tarelho, L. A. C., Oduber, F. I., and Alves, C.: Particulate and gaseous emissions from charcoal combustion in barbecue grills, Fuel Processing Technology, 176, 296-306, 10.1016/j.fuproc.2018.03.004, 2018.

Wang, H., Li, Y., Liu, Y., Lu, X., Zhang, Y., Fan, Q., Shen, C., Lai, S., Zhou, Y., Zhang, T., and Yue, D.: Underappreciated contributions of biogenic volatile organic compounds from urban green spaces to ozone pollution, Atmospheric Chemistry and Physics, 25, 5233-5250, 10.5194/acp-25-5233-2025, 2025.

Zhu, Q., Huang, X.-F., Cao, L.-M., Wei, L.-T., Zhang, B., He, L.-Y., Elser, M., Canonaco, F., Slowik, J. G., Bozzetti, C., El-Haddad, I., and Prévôt, A. S. H.: Improved source apportionment of organic aerosols in complex urban air pollution using the multilinear engine (ME-2), Atmospheric Measurement Techniques, 11, 1049-1060, 10.5194/amt-11-1049-2018, 2018.